van Laar Correlation

Another two-parameter excess Gibbs energy model was developed from an expansion of \((RTx_1x_2)/G^E\) instead of \(G^E/RTx_1x_2\). The end results are:

\[
\frac{G^E}{RTx_1x_2} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2}
\]

for the excess Gibbs energy and:

\[
\ln \gamma_1 = A'_{12}\left(1 + \frac{A'_{12}x_1}{A'_{21}x_2}\right)^{-2}
\]

(12.17a)

\[
\ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}
\]

(12.17b)

for the activity coefficients.

Note that: as \(x_1 \to 0\), \(\ln \gamma_1^\infty \to A'_{12}\)

and as \(x_2 \to 0\), \(\ln \gamma_2^\infty \to A'_{21}\)
Example 2 (Problem 5, Practice Problem Set #4)

P5. Vapour liquid data for the system 1,4 dioxane(1)/ethylbenzene(2) at 85 °C are provided below. From these data obtain estimates of the van Laar coefficients (estimates based on smoothly drawn curves on the enclosed graph paper are sufficient). Estimate values of $P-x_1-y_1$ for $x_1=0.5$ based on these parameter values. Table 2: VLE data for the system 1,4 dioxane/ethylbenzene at 85 °C

<table>
<thead>
<tr>
<th>$P$ (kPa)</th>
<th>$x_1$</th>
<th>$y_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23.4</td>
<td>0.065</td>
<td>0.15</td>
</tr>
<tr>
<td>35.2</td>
<td>0.29</td>
<td>0.55</td>
</tr>
<tr>
<td>41.6</td>
<td>0.44</td>
<td>0.7</td>
</tr>
<tr>
<td>52.4</td>
<td>0.78</td>
<td>0.91</td>
</tr>
<tr>
<td>57.8</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Local Composition Models

Unfortunately, the previous approach cannot be extended to systems of 3 or more components. For these cases, local composition models are used to represent multi-component systems.

- Wilson’s Theory
- Non-Random-Two-Liquid Theory (NRTL)
- Universal Quasichemical Theory (Uniquac)

While more complex, these models have two advantages:

- the model parameters are temperature dependent
- the activity coefficients of species in multi-component liquids can be calculated using information from binary data.
Wilson’s Equations for Binary Solution Activity

A versatile and reasonably accurate model of excess Gibbs Energy was developed by Wilson in 1964. For a binary system, \( G^E \) is provided by:

\[
\frac{G^E}{RT} = x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21})
\]  

(12.18)

where

\[
\Lambda_{12} = \frac{V_2}{V_1} \exp\left[\frac{-a_{12}}{RT}\right], \quad \Lambda_{21} = \frac{V_1}{V_2} \exp\left[\frac{-a_{21}}{RT}\right]
\]  

(12.24)

\( V_i \) is the molar volume at \( T \) of the pure component \( i \).

\( a_{ij} \) is determined from experimental data.

The notation varies greatly between publications. This includes,

\( a_{12} = (\lambda_{12} - \lambda_{11}) \), \( a_{21} = (\lambda_{12} - \lambda_{22}) \) that you will encounter in Holmes, M.J. and M.V. Winkle (1970) *Ind. Eng. Chem.* 62, 21-21.
Wilson’s Equations for Binary Solution Activity

Activity coefficients are derived from the excess Gibbs energy using the definition of a partial molar property:

\[
RT \ln \gamma_i = \overline{G_i}^E = \left. \frac{\partial nG^E}{\partial n_i} \right|_{T,P,n_j}
\]

When applied to equation 11.16, we obtain:

\[
\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left( \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \tag{12.19a}
\]

\[
\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) - x_1 \left( \frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right) \tag{12.19b}
\]
Wilson’s Equations for Multi-Component Mixtures

The strength of Wilson’s approach resides in its ability to describe multi-component (3+) mixtures using binary data.

- Experimental data of the mixture of interest (ie. acetone, ethanol, benzene) is not required
- We only need data (or parameters) for acetone-ethanol, acetone-benzene and ethanol-benzene mixtures

The excess Gibbs energy for multicomponent mixtures is written:

\[ \frac{G^E}{RT} = -\sum_i x_i \ln(\sum_j x_j \Lambda_{ij}) \]  \hspace{1cm} (12.22)

and the activity coefficients become:

\[ \ln \gamma_i = 1 - \ln \sum_i x_j \Lambda_{ij} - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \]  \hspace{1cm} (12.23)

where \( \Lambda_{ij} = 1 \) for \( i=j \). Summations are over all species.
Wilson’s Equations for 3-Component Mixtures

For three component systems, activity coefficients can be calculated from the following relationship:

\[
\ln \gamma_i = 1 - \ln(x_1 \Lambda_{i1} + x_2 \Lambda_{i2} + x_3 \Lambda_{i3}) - \frac{x_1 \Lambda_{1i}}{x_1 + x_2 \Lambda_{12} + x_3 \Lambda_{13}} \\
- \frac{x_2 \Lambda_{2i}}{x_1 \Lambda_{21} + x_2 + x_3 \Lambda_{23}} \\
- \frac{x_3 \Lambda_{3i}}{x_1 \Lambda_{31} + x_2 \Lambda_{32} + x_3}
\]

Model coefficients are defined as \((\Lambda_{ij} = 1 \text{ for } i=j)\):

\[
\Lambda_{ij} = \frac{V_j}{V_i} \exp \left[ -\frac{a_{ij}}{RT} \right]
\]
Comparison of Liquid Solution Models

Activity coefficients of 2-methyl-2-butene + n-methylpyrrolidone.

Comparison of experimental values with those obtained from several equations whose parameters are found from the infinite-dilution activity coefficients.
(1) Experimental data.
(2) Margules equation.
(3) van Laar equation.
(4) Scatchard-Hamer equation.
(5) Wilson equation.
We now have the tools required to describe and calculate vapour-liquid equilibrium conditions for even the most non-ideal systems.

1. Equilibrium Criteria:
   ➢ In terms of chemical potential
     \[ \mu_i^v = \mu_i^l \]
   ➢ In terms of mixture fugacity
     \[ \hat{f}_i^v = \hat{f}_i^l \]

2. Fugacity of a component in a non-ideal gas mixture:
   \[ \hat{f}_i^v (T, P, y_1, y_2, \ldots, y_n) = y_i \hat{\phi}_i^v (T, P, y_1, y_2, \ldots, y_n) P \]

3. Fugacity of a component in a non-ideal liquid mixture:
   \[ \hat{f}_i^l (T, P, x_1, x_2, \ldots, x_n) = x_i \gamma_i (T, P, x_1, x_2, \ldots, x_n) \hat{f}_i^l \]
   \[ = x_i \gamma_i (T, P, x_1, x_2, \ldots, x_n) \phi_i^{sat} P_i^{sat} \exp \left[ \frac{V_i (P - P_i^{sat})}{RT} \right] \]
γ, φ Formulation of VLE Problems

To this point, Raoult’s Law was only description we had for VLE behaviour:
\[ y_i P = x_i P_{i\text{sat}} \]

We know that calculations based on Raoult’s Law do not predict actual phase behaviour due to over-simplifying assumptions.

Accurate treatment of non-ideal phase equilibrium requires the use of mixture fugacities. At equilibrium, the fugacity of each component is the same in all phases. Therefore,

\[ \hat{f}_i^v = \hat{f}_i^l \]

or,
\[ y_i \phi_i P = x_i \gamma_i \phi_{i\text{sat}} P_{i\text{sat}} \exp \left[ \frac{V_i (P - P_{i\text{sat}})}{RT} \right] \]
determines the VLE behaviour of non-ideal systems where Raoult’s Law fails.
Non-Ideal VLE to Moderate Pressures

A simpler expression for non-ideal VLE is created upon defining a lumped parameter, $\Phi$.

$$
\Phi_i = \frac{\hat{\phi}_i^v}{\phi_i^{sat}} \exp \left[ -\frac{V_i^l (P - P_i^{sat})}{RT} \right]
$$

The final expression becomes,

$$
y_i \Phi_i P = x_i \gamma_i P_i^{sat} \quad (i = 1,2,3,\ldots,N)
$$

To perform VLE calculations we therefore require vapour pressure data ($P_i^{sat}$), vapour mixture and pure component fugacity correlations ($\Phi_i$) and liquid phase activity coefficients ($\gamma_i$).
Non-Ideal VLE to Moderate Pressures

Sources of Data:
1. Vapour pressure: Antoine’s Equation (or similar correlations)

\[ \ln P_i^{\text{sat}} = A_i - \frac{B_i}{T + C_i} \]  

2. Vapour Fugacity Coefficients: Viral EOS (or others)

\[ \Phi_i = \exp \left[ \frac{B_{ii}(P - P_i^{\text{sat}}) + 0.5P \sum_j \sum_k y_jy_k(2\delta_{ji} - \delta_{jk})}{RT} \right] \]  

3. Liquid Activity Coefficients
   - Binary Systems - Margules, van Laar, Wilson, NRTL, Uniquac
   - Ternary (or higher) Systems - Wilson, NRTL, Uniquac